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Partitioning of chemical contaminants to microplastics: Sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation☆

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ABSTRACT

There is an increasing awareness of the threats posed by the worldwide presence of microplastics (MPs) in the environment. Due to their high persistence, MPs will accumulate in the environment and their quantities tend to increase with time. MPs end up in environments where often also chemical contaminants are present. Since the early 2000s, the number of studies on the sorption of chemicals to plastic particles has exponentially increased. The objective of this study was to critically review the literature to identify the most important factors affecting the sorption of chemical contaminants to MPs. These factors include the physicochemical properties of both the MPs and the chemical contaminants as well as environmental characteristics. A limited number of studies on soil together with an increased notion of the importance of this compartment as a final sink for MPs was observed. Therefore, we assessed the distribution of model chemicals (two PCBs and phenanthrene) in the soil compartment in the presence of MPs using a mass balance model. The results showed a high variation among chemicals and microplastic types. Overall, a higher partitioning to MPs of chemical contaminants in soil is expected in comparison to aquatic environments. As sorption to a large extent determines bioavailability, the effects of combined exposure to chemicals and MPs on the toxicity and bioaccumulation in biota are discussed. Finally, some considerations regarding sorption and toxicity studies using MPs are given.

1. Introduction

Nowadays, one of the greatest concerns regarding environmental contamination is the presence of plastics in diverse ecosystems (Eriksen et al., 2014). Plastics are versatile, low-cost materials that can be used in a wide number of applications and products. 'Plastic' is a generic term used for both natural and synthetic polymers. However, synthetic materials account for >90% of the plastics produced, such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polystyrene (PS) (Andrady & Neal, 2009). Moreover, these materials are highly persistent, being the most abundant anthropogenic waste. Until the year 2015, it is estimated that approximately 6300 Mt of plastic waste has been generated globally (Geyer et al., 2017). Only about 20% of this waste was recycled or incinerated, while 80% is either accumulated in landfills or released to natural environments (Geyer et al., 2017).

Regarding the plastic waste disposed in the environment, recently special attention has been drawn to microplastics (MPs). MPs are defined as plastic particles with sizes ranging from 1 μm to 5 mm (Thompson et al., 2004). They can be divided into primary and secondary microplastics (Arthur et al., 2009). Primary MPs are produced and discharged to the environment in the micro or milli-scale size (such as the beads used in cosmetics). Secondary MPs are the result of the breakdown of larger plastic fragments after being introduced into the environment (Arthur et al., 2009), normally caused by UV radiation and physical abrasion.

For many years, most studies were conducted mainly on marine environments, reporting alarming quantities of microplastics. For instance, estimations on the total amount of MPs present in oceans range from 15 to 51 trillion particles (van Sebille et al., 2015). The

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number of studies on MPs in freshwater, freshwater sediment and soil compartments is increasing, though it is still much lower than the number of marine studies. These compartments are suggested to be a very important sink of MPs. It is estimated that per year up to 0.9 million metric tons of MPs are retained in the continental environments, while up to 0.11 million metric tons reach the oceans (Horton et al., 2017).

With the high accumulation in the environment, MPs are not only potential contaminants but they can also act as an extra compartment for the partitioning of chemicals. The partitioning and sorption between compartments is extremely important as it determines the fate and the bioavailability of chemical compounds. The chemical, also named sorbate, is distributed depending on its affinity for the sorbent phases. Therefore, the distribution of chemical contaminants in the environment depends directly on their physicochemical properties and on environmental factors.

Even though the first reports on contaminant sorption to plastic particles dated back to the 1970s and 1980s (Mato et al., 2001, and references cited therein), only in the early 2000s this subject started to be investigated more intensively (Mato et al., 2001; Endo et al., 2005). These studies observed high concentrations of chemical contaminants on MPs collected in marine environments, indicating that sorption to MPs was likely to be a relevant issue. Consequently, partitioning studies under laboratory conditions were found necessary to understand the sorption of chemical contaminants to microplastics. The number of studies in this field is exponentially increasing. A search on the Web of Science database for "microplastics sorption" produced 91 results, with more than half of the papers being published only between 2018 and 2019 (Figure SI-1). With the increasing number of studies on the sorption of chemicals to MPs, this paper aims at critically reviewing the literature to gather information on the relevant mechanisms and factors driving the sorption process. Even though MPs can also release additives, like plasticizers, to the environment, this review will focus only on the sorption/desorption of chemical contaminants (aside from the additives) from the environment to MPs.

First, a brief summary of the theory of sorption isotherms and sorption kinetic models will be presented, followed by an overview of the mechanisms responsible for the affinity between MPs and chemicals, and the possible influencing factors. Since a few studies have been conducted in the field, the differences between laboratory and field data will also be discussed.

Throughout the review process, it was evident that studies conducted on soil are lacking. In order to fill this gap, we used a mass balance model to determine the importance of MPs as a compartment for chemical distribution in soils. Two PCB congeners and phenanthrene were used as model chemicals and results are compared with those obtained for other environmental compartments.

In addition, we review the toxicity outcomes of combined exposures to MPs and chemical contaminants. Although a number of studies used biomarkers (Browne et al., 2013; O'Donovan et al., 2018; Brandts et al., 2018; Batel et al., 2016) or assessed neuro- and genotoxicity (O'Donovan et al., 2018; Zhang et al., 2019b), this review will focus more on the studies that allow relating toxicity to the sorption to MPs and help understanding its importance for the bioavailability of chemical compounds. Finally, we will discuss some considerations to be taken into account when performing sorption and toxicity experiments with MPs.

2. Sorption isotherms and sorption kinetics

The terms 'partitioning' and 'sorption' are often used as synonyms to describe the transfer of chemicals between phases. Even though only 'partitioning' refers to a process involving any phase, it may also be used as a synonym for absorption in some fields (Endo & Koelmans, 2016). To avoid misleading interpretations, the terms 'partitioning', 'sorption', and 'ab/adsorption' will be used throughout this review as defined below.

Sorption is the process of mass transfer of a chemical from a liquid (or gaseous) phase to a solid phase. Environmental media can be very complex in their composition, having many phases for the distribution of chemical contaminants. For example, aquatic phases have suspended sediments, dissolved and particulate organic matter, while soils and sediments also have dissolved organic matter and the porewater. Based on the definition given by Endo & Koelmans (2016), we will use partitioning to refer to scenarios involving other phases of the media (e.g., bridging effect involving humic acids). And sorption will be used when the process is clearly restricted to transfer between the liquid phase and MPs (as the solid phase). Sorption includes the attachment to surfaces (adsorption) and the assimilation into the bulk of a matrix (absorption). The detachment from the solid phase is named desorption. Both absorption and adsorption can happen concurrently and it can be difficult to discriminate one process from the other (Endo et al., 2008; Dąbrowski, 2001). For this reason, we have chosen to use the term sorption, regardless of the original term used by the authors of the cited studies.

The partitioning of chemicals between two phases is a dynamic process and a state of equilibrium is reached when the concentrations in both phases are constant. At equilibrium, isotherm equations can be applied in order to obtain equilibrium constants (Tables SI–1). These are empirical equations, and many authors have successfully used isotherms to determine the sorption of different chemicals to MPs.

In a linear isotherm model, the sorption distribution coefficient (K_d) is the ratio between the concentration in the solid phase (i.e., amount of chemical per unit mass of MP) and the equilibrium concentration in the liquid phase. The relationship between solid and liquid phases however, might not be linear, which asks for the use of non-linear sorption isotherms. A number of theories have been developed since the first studies on sorption processes (Dąbrowski, 2001), but two non-linear isotherms are mostly used. The Freundlich isotherm, which has been widely applied for chemical sorption to MPs, describes the sorption to heterogeneous surfaces. In this model, the occupancy of high energy sites occurs, followed by the occupancy of low energy sites (Guo et al., 2018). Alternatively, the Langmuir isotherm has been applied, for considering homogenous surfaces in which the sorbate will have one-layer (monolayer) coverage and with a finite number of sorption sites. Extensions of the Langmuir model (Extended Langmuir isotherm and Interaction Factor Model) can be used for assessing the sorption of two sorbates simultaneously, as used by Bakir et al. (2012) to study the sorption of phenanthrene and DDT to PVC (see Bakir et al. (2012) for the equations).

It is also possible to determine K_d values taking into account other phases, such as dissolved organic matter as done by Seidensticker et al. (2017). These authors used a linear isotherm that includes the partitioning coefficient between organic matter and liquid phase (K_{DOM}) and the concentration of dissolved organic matter. This approach should be encouraged as unifying different equilibrium constants to a single equation can produce more realistic values than using separate equations.

In addition to the equilibrium partitioning coefficients, it is also important to understand the rate of the sorption process, by using empirical kinetics equations (Tables SI–1). Kinetic models are good for evaluating the sorption efficiency, understanding rate-limiting steps, and identifying sorption mechanisms (Febrianto et al., 2009). The most commonly applied kinetic models are first order (or Lagergren equation) and second order models, which assume

that the sorbate interacts with one and two types of adsorption sites (i.e., one-site or two-site occupancy adsorption), respectively (Rudzinski & Plazinski, 2006). It is also possible to add the desorption rate (K_{-1}) in the first-order equation, as in Turner & Holmes (2015) and Müller et al. (2018).

Beside the first and second order kinetics equations, which are controlled by the reactions occurring on the surface, the intra-particle diffusion equation corresponds to a diffusion-controlled process (Simonin, 2016). This model has also been used in kinetic studies on MPs. It assumes that sorption to the external surface and diffusion to interior pores occur in a multiple step process (Markandeya & Kisku, 2015). Also, for spherical pellets, the diffusion model based on Fick's second law can be applied (Karapanagioti et al., 2010; Fries & Zarfl, 2012), which considers the radius of the pellet.

The interpretation of the results is crucial in sorption studies. So firstly, the assumptions of each model should not be ignored. For example, using the isotherm equations mentioned in the Supporting Information, equilibrium must be reached. For non-equilibrium conditions, the apparent distribution coefficient (K_{da}) should be used (Grathwohl, 1998). Secondly, to decide the best fitting model, many studies compared R^2 values of linearized Freundlich and Langmuir equations (Li et al., 2018; Liu et al., 2018; Wang & Wang, 2018b; Zhan et al., 2016; Wu et al., 2019). Since these equations have different number of parameters, such comparison however, is not appropriate. One option is to conduct the extra sum of squares F-test, if models are nested (i.e., one model containing all the parameters in the other model) (Motulsky & Ransnas, 1987). This is the case for the first order and reversible first order models. For non-nested models, the Akaike's Information Criterion (AIC) can be used (Motulsky & Christopoulos, 2004). For instance, Hüffer & Hofmann (2016) applied AIC and root mean square error (RMSE) when comparing isotherm models of organic compounds to different MP materials. When comparing the linearized versions of kinetics equations, comparisons should be made with original scales and not transformed scales (i.e., linear version of kinetic equations) (Simonin, 2016). As pointed out by Tran et al. (2017), the linear version of the kinetic equations will also produce higher R^2 values in comparison to the original, nonlinear equations. This can mislead the results, if R^2 of the linear version is used and a lower R^2 of the original equations is ignored. The same can be applied to isotherms. Wang & Wang (2018a) observed a high R^2 for the linearized Freundlich equation ($R^2 = 0.96$), even though the data did not yield a good fit to the Freundlich model.

3. Mechanisms of the sorption of chemicals to microplastics

3.1. Hydrophobic and electrostatic forces

The sorption process is intrinsically related to the physio-chemical properties of both the sorbate and the sorbent. Therefore, the mechanism depends on the interactions between sorbate and sorbent, which can be dominated by a specific interaction or even be a contribution of different interactions.

Hydrophobic and electrostatic interactions are the predominant mechanisms for the sorption of many chemical contaminants (Mato et al., 2001; Xu et al., 2018b; Wang et al., 2015; Guo et al., 2018; Llorca et al., 2018; Wu et al., 2019). Hydrophobic interactions relate to the attraction of non-polar (or slightly polar) molecules to the non-polar MP surface, and are considered to be one of the main mechanisms governing the sorption of hydrophobic organic chemicals to MPs (Wang et al., 2015; Du et al., 2014; Mato et al., 2001; Hüffer & Hofmann, 2016; Liu et al., 2018). More hydrophilic MPs, such as polyamides (PA), however, seem to have higher sorption affinity for hydrophilic organic compounds, such as antibiotics (Li et al., 2018) and 17β-Estradiol (Liu et al., 2019). Similarly, lower sorption of non-polar organic contaminants to PA was observed in comparison to PE, PVC and PS (Hüffer & Hofmann, 2016), while lower sorption of phenanthrene to nylon than to PE was attributed to hydrophilic functional groups in nylon (Wang et al., 2018).

Electrostatic interactions, on the other hand, are caused by the attraction of oppositely charged molecules or repulsion of similarly charged molecules. In general, MP surfaces can become negatively charged due to the pH of point of zero charge (pH_{pzc}) being lower than most environmental pHs (Li et al., 2018; Xu et al., 2018b; Zhang et al., 2018a). As a result, the negative net charges on the MP surface (such as PE, PP, PS and PVC) are likely to attract positively charged species (Guo et al., 2018; Wang et al., 2015; Xu et al., 2018a; Razanajatovo et al., 2018). For chemicals existing mainly in the anionic form, however, the repulsion by the MP surface is likely to reduce the sorption (Xu et al., 2018a; Razanajatovo et al., 2018; Wu et al., 2019). Therefore, whether attraction or electrostatic repulsion occur depends on media pH, pH_{pzc} of the polymer and the acid dissociation constant (pKa) of the chemical contaminant (Razanajatovo et al., 2018).

3.2. Other mechanisms

Hydrogen bonds are specific weak electrostatic interactions, involving hydrogen ion H^+, and can affect the sorption of polymers when proton donor and proton acceptor groups are involved. Li et al. (2018) found that polyamide (PA) had a greater sorption capacity for a group of antibiotics than did PVC, PE, PS and PP. This was attributed to the hydrogen bond caused by the proton donor characteristic of the amide group in PA.

Other interactions also promote the sorption of chemicals onto MPs, including van der Waals and pi-pi interactions. van der Waals forces are weak interactions occurring between molecules not involving covalent or ionic bonding, while pi-pi interactions are attraction forces between aromatic molecules. Thus, aliphatic polymers, such as PE and PVC, undergo van der Waals interactions, while aromatic polymers, such as PS, can undergo pi-pi interactions (Hüffer & Hofmann, 2016; Müller et al., 2018; Hüffer et al., 2018). As pi-pi interactions are stronger, the K_f value was one order of magnitude higher for the sorption of aromatic chemicals to PS than to PE, PA and PVC (Hüffer & Hofmann, 2016).

4. Influence factors on chemical contaminant sorption to MPs

4.1. MP and chemical contaminant characteristics

Several key factors have been found to affect the sorption of chemicals to MPs, including the characteristics of both MPs and sorbates as well as the properties of the medium. For MPs, the type of material determines the interactions that occur on the MP surface (as discussed above), and sorption capacity can vary by several orders of magnitude among materials (Teuten et al., 2007; Brennecke et al., 2016; Velzeboer et al., 2014; Hüffer & Hofmann, 2016). However, the type of MP material should not be the only characteristic to be taken into account, as other characteristics have been found to interfere with the sorption process.

Among the most relevant characteristics studied are MP size and shape. It should be highlighted, however, that size and shape may affect adsorption, but are less important in the absorption process, as absorption does not depend on the availability of sorption sites on the surface. In the adsorption process, as a general rule, particles presenting a higher area-to-volume ratio are expected to have a higher adsorption capacity, such as the smaller sized particles (Liu

et al., 2018; Velzeboer et al., 2014; Zhan et al., 2016; Wang et al., 2018) and particles with irregular shapes (Brennecke et al., 2016). For instance, the equilibrium concentration (Qe) of PCBs increased from ~60 to 210 μg/g with decreasing PP sheet size from 5 to 0.18 mm (Zhan et al., 2016). The larger Brunauere-Emmette-Teller (BET) surface area of high density polyethylene (HDPE) (6.9 m^2/g) also resulted in a higher sorption capacity for pyrene compared with PS (2.3 m^2/g) and PVC (1.8 m^2/g) (Wang & Wang, 2018a). Llorca et al. (2018) concluded that MP size affected the sorption process. They used PS and PE MPs with particle sizes of 10 and 3–16 μm, respectively. The overlap of particle sizes however, makes it difficult to believe that any difference in particle size could be responsible for the difference in sorption.

Nevertheless, MP area effect can be overruled by other characteristics or if absorption is involved, making its influence negligible (Hüffer & Hofmann, 2016; Xu et al., 2018b). Xu et al. (2018b) found a higher sorption capacity of tetracycline for PS than PE, even though PE had a higher surface area (0.23 m^2/g) and smaller size (150 μm) compared with PS (0.05 m^2/g, <280 μm). This result was attributed to the pi-pi interactions between tetracycline and PS. Similarly, particle size and surface area could not explain the differences in sorption of organic chemicals to PA, PE, PS, and PVC MPs due to the greater influence of hydrophobic interactions (Hüffer & Hofmann, 2016). Moreover, the size of pores in the MPs will be crucial, as small pores enable the interaction of the sorbate with the sorbent surface, leading to the formation of monolayer adsorption, while larger pores allow mono- and multilayer formation (Dąbrowski, 2001). Li et al. (2018) found that PA had a greater sorption capacity for antibiotics than PVC, PE, PS and PP, which was partially attributed to surface pores observed by SEM images (together with the formation of hydrogen bonds). Nevertheless, thye authors should be cautious when speculating on the influence of pore size. Wang et al. (2015) concluded that benzene rings of the PS structure decreased the free volume between atoms of polymer chains by steric effects, and no sorption of perfluorooctanesulfonate (PFOS) could be detected. This explanation is, however, contradicted by the fact that perfluorooctanesulfonamide (FOSA), which has the same chain length and similar molecular weight, did sorb to PS MPs, and therefore steric hindrance could not explain these results.

Another major characteristic affecting sorption is the degree of crystallinity of the polymers, which is related to the arrangement of the principal carbon chain. A higher degree of crystallinity indicates that the polymeric chain is more ordered, while more disordered chains result in a greater proportion of amorphous regions. Due to the size and complexity, the polymer chains are often semi-crystalline, interposing crystalline and amorphous regions.

In the crystalline region, a high energy is necessary for absorbing chemicals, while in amorphous regions the atoms can move more freely favoring chemical absorption (Callister, 2001). The amorphous region will present different states depending on the temperature. This is known as glass transition temperature (T_g). At environmental temperatures below T_g, the amorphous region will be in the rubbery state, and above T_g in the glass state. This is important because in the rubbery state the carbon chain can move, while in the glassy state movement is restricted (Endo & Koelmans, 2016). Therefore, the higher sorption of chemicals is observed in rubbery polymers (Wu et al., 2016; Guo et al., 2012; Rochman et al., 2013b). Pyrene sorption was higher to PE than to PS and PVC, which was related to surface area, but also because PE is a semi-crystalline polymer, while PS and PVC are glassy polymers with large crystalline regions (Wang & Wang, 2018a). In accordance with Bakir et al. (2012), Seidensticker et al. (2018) and Zuo et al. (2019), the main sorption mechanism for rubbery polymers is partitioning, while for glassy polymers both partitioning and pore-filling are involved. These characteristics can be observed from the sorption isotherm: glassy polymers present non-linear isotherms with higher competition for the sorption sites, while rubbery polymers show linear sorption isotherms with lower competition (Bakir et al., 2012; Endo & Koelmans, 2016).

However, as mentioned above for MP size and shape, crystallinity alone may not always explain the differences in sorption among MPs. The K_d of FOSA, for instance, was not correlated to crystallinity of PE, PS and PVC, and other polymer characteristics were found to be more important (Wang et al., 2015). Also Li et al. (2018) found that the degree of crystallinity of five different polymers (e.g., PE, PP, PA, PS and PVC) failed to explain their sorption capacity for antibiotics.

The characteristics of the sorbate are also equally important in defining its sorption to MPs, affecting both the equilibrium time (Zhan et al., 2016) and sorption capacity (Zhan et al., 2016; Velzeboer et al., 2014). For organic chemicals, hydrophobicity and molecular weight may help explaining the sorption. Due to the hydrophobic nature of the MP surface, sorption coefficients for organic chemicals may be correlated to their octanol-water partition coefficient (K_{ow}) (Llorca et al., 2018; Wu et al., 2016; Beckingham & Ghosh, 2017; Li et al., 2018; Zuo et al., 2019). When diffusion is the rate-limiting process, the molecular weight however, becomes more important than K_{ow} as diffusion is hampered by the increase of molecular size (Fries & Zarfl, 2012). Similarly, for hydrophilic chemicals, molecular size (i.e., carbon-chain length) can be more important than hydrophobic interactions (Llorca et al., 2018). When evaluating sorption of 19 polar and non-polar chemicals on PS and PE MPs using a pH-dependent partitioning coefficient, Seidensticker et al. (2018) observed that overall neutral species had a stronger sorption in comparison to charged species. However, some charged compounds can also have strong hydrophobic interactions with MPs, such as nonylphenol and diazinon.

In the case of metals, chemical speciation can be a good approach for predicting their sorption to MPs. Sorption of metals can be driven by the formation of free cation species and organo-metallic complexes in the medium. Free cations are likely to react with charged regions of negative MP surfaces which can be created by the adsorption of organic molecules (Ashton et al., 2010; Holmes et al., 2014, 2012) or due to the presence of plastic additives (Ashton et al., 2010). Organo-metallic complexes, on the other hand, can interact with the neutral areas of MP surfaces due to hydrophobic interactions (Holmes et al., 2012).

4.2. Medium characteristics

Medium proprieties may also influence sorption by altering MP surface charge and the speciation of chemicals. This is especially true when electrostatic interactions are involved, as pH, ionic strength and salinity can considerably affect the electrostatic interactions, or when surface processes are predominant. For instance, NaCl and $CaCl_2$ levels did not affect the hydrophobic sorption of FOSA to PE, but it did affect the sorption of PFOS, indicating a predominance of electrostatic interactions in the latter case and therefore a greater influence of the ionic chemical composition of the media (Wang et al., 2015).

The effect of pH is rather complex, and a non-linear relationship with sorption is commonly observed. The sorption of tylosin to PVC and PS increased with increasing pH up to pH 7.1, due to the electrostatic interactions of the positively charged tylosin with the negative surface charge on the polymers (Guo et al., 2018). For pH > 7.1, it was expected that sorption would keep increasing as the polymers become more negatively charged, however, sorption decreased. The authors believe that electrostatic forces decreased at higher pH due to a decrease of the cation species of tylosin and the subsequent prevalence of hydrophobic forces. The sorption of

tetracycline to PE, PP and PS peaked at pH 6 and was dominated by hydrophobic forces, however, at higher or lower pH values, sorption was rather dominated by electrostatic interactions (Xu et al., 2018b). Indeed, pH effect is dependent on the chemical speciation. Sorption of the antibiotic oxytetracycline to weathered PS foam peaked at pH 5 due to the greater proportion of its cationic form in the solution (Zhang et al., 2018a). In this case, electrostatic repulsion to the negatively charged MP surface decreased and sorption was enhanced. It indicates that sorption mechanism was regulated by the electrostatic forces, and when it was minimal at pH 5, H-bonding between sorbate and sorbent was the predominant mechanism.

The relationship between pH and ionic strength and its effects on the sorption of atrazine and 4-(2,4-dichlorophenoxy) butyric acid (DB) in soils has been presented in Hüffer et al. (2019). At pH 3, DB is mostly in nonionic form (pKa of 4.95) and K_d values were not influenced by the presence of Ca^{2+}. However, at pH 7, the bridging effects of Ca^{2+} is more evident, and K_d increased with increasing $CaCl_2$ levels, since DB is fully deprotonated and PE and soil particles are negatively charged. Atrazine, on the other hand, has a small proportion (5%) of cations at pH 3, but is neutral at pH 7. Therefore, at pH 3 a decrease in K_d was observed with increasing ionic strength, as Ca^{2+} competes with the cations for the sorption sites on PE surface. At pH 7, K_d did not change with increasing Ca^{2+} levels, once atrazine is neutral and no competition occurs (Hüffer et al., 2019).

For metals, the pH influence is metal-dependent (Holmes et al., 2014; Turner & Holmes, 2015). For metals producing cationic species (e.g. Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}), higher sorption capacities were observed with increasing pH, as there is a decline in the relative abundance of free ions (Holmes et al., 2014; Turner & Holmes, 2015). For Cr, sorption decreased with increasing pH, suggesting that Cr speciation produced negative forms like $HCrO^{4-}$ and CrO_4^{2-} (Holmes et al., 2014; Turner & Holmes, 2015). For other metals, such as Cu and Hg, MP sorption showed no clear relation to pH which was attributed to the low free ion concentration and the sorption of organic complexes with neutral charge (Holmes et al., 2014).

When comparing fresh and seawater, sorption of perfluoroalkyl substances to PE, PS and polystyrene carboxylate (PS-COOH) decreased with increasing pH and found to be lower in seawater (Llorca et al., 2018). Even though the presence of bivalent cations could result in a bridging effect (e.g., negatively charged MP and sorbate bridged by Ca^{2+} and Mg^{2+}), the pH effect was predominant and generally sorption to MPs decreased in seawater in comparison to freshwater. The mechanisms for decreasing sorption with increasing the salinity include the competition between ions for sorption sites (Liu et al., 2018; Zhang et al., 2018a) and electrostatic forces (Li et al., 2018). The latter can be caused by the production of negative species of a sorbate with increasing salinity, which causes electrostatic repulsion to the negative MP surface (Li et al., 2018). Nevertheless, salinity may also increase sorption depending on the chemical contaminant and even MP properties. Besides the bridging effect mentioned above, the salting out effect can increase sorption to MPs by decreasing the solubility of the chemical contaminant (Wu et al., 2016; Liu et al., 2019).

Bakir et al. (2014b) and Zuo et al. (2019) found conflicting results when studying pH effects on phenanthrene sorption to MPs with different degree of crystallinity. Zuo et al. (2019) found that phenanthrene sorption was more affected by salinity when the MPs were in the rubbery state (PE) than in the glass state (PS), while Bakir et al. (2014b) observed no effect of pH on phenanthrene sorption to PE and PVC (glassy). Taking into consideration the discussion in the previous section, pH would be expected to have a low influence on the sorption to MPs in a rubbery state, as absorption is the main mechanism.

As mentioned above, organic matter (OM) can react with metals and therefore play an important role in the sorption of metals and metallic species to MPs. Generally, neutral organo-metallic complexes are formed, with higher hydrophobicity compared to the free ions, and thus favoring the sorption to hydrophobic MPs (Holmes et al., 2012). However, it is also possible that OM decreases the free ion concentration in the medium, resulting in lower sorption. This should probably be treated on a case-by-case basis, with particular metals and/or OM composition and concentration giving different outcomes.

For organic chemicals, the presence of OM is likely to decrease the sorption to MPs, as small and dissolved OM (DOM) can also bind the chemicals and compete with MPs (Xu et al., 2018b; Llorca et al., 2018; Zuo et al., 2019). In accordance with Wu et al. (2016), the higher affinity of non-polar chemicals to organic matter will result in a decreased sorption to MPs, while less influence of DOM will be observed for polar chemicals. On the other hand, cationic or zwitterionic species can bind to MPs bridged by deprotonated (OH^-) humic acids, as shown for the sorption of oxytetracycline to PS foam MPs (Zhang et al., 2018a). In this study, cationic species of oxytetracycline bound to deprotonated sites of humic acid via H-bonding and cation exchange. The presence of DOM was also found to be less significant when absorption is the dominant process (Velzeboer et al., 2014), as it has greater effects on the processes occurring on the surface, or when the MPs are nonporous, as no pore blockage by OM occurs (Liu et al., 2019).

5. Comparison between field and laboratory studies

Most sorption studies with MPs are conducted in the laboratory under controlled conditions. In the field, environmental conditions can vary considerably, such as sorbate concentration, temperature and medium composition. In addition, MP degradation, biofilm formation, and the presence and possible competition of sorbates can also affect the processes and rates of the sorption of chemicals to MPs. Interestingly, several studies have been successful in fitting sorption isotherms and kinetics equations to samples collected from the field (Rochman et al., 2013a, 2014; Ashton et al., 2010; Wang et al., 2018). This is an indication that, even though not all assumptions are fulfilled, the current models are able to predict the sorption of chemicals to MPs also under field conditions.

One main difference between lab and field experiments is the equilibration time (Rochman et al., 2014; Zhan et al., 2016; Holmes et al., 2012). Equilibrium is reached much faster under lab conditions, and for the same sorbate equilibrium can be reached within hours or days in the lab, while it takes several months in the environment (Zhan et al., 2016; Rochman et al., 2014). Possible explanations include the lower sorbate concentrations in the environment (Rochman et al., 2014) and the constant agitation usually applied in lab experiments (Zhan et al., 2016).

Once in the environment, the aging or weathering of MPs can lead to several modifications of the MP surface. For example, MPs can be covered by fouling material which is composed of organic matter and biological material (i.e., biofilm). Fouling material can change the density of MPs (Bakir, 2014b) or even act as an additional sorbent (Endo et al., 2005).

Aged and weathered MPs undergo degradation, including photo-degradation, biodegradation, thermo-degradation and hydrolysis (Andrady, 2011). Aging and weathering can result in a higher sorption capacity by increasing surface area (Mato et al., 2001; Zhang et al., 2018a) and pore area of the aged MPs (Zhang et al., 2018a). Photo-oxidation, the predominant degradation process of polymers (Feldman, 2002), results in the formation of carbonyl groups, which increase the polarity of the surface. Therefore, photo-oxidation can increase the sorption of polar

chemicals (Holmes et al., 2012), while decreasing the sorption of non-polar chemicals (Hüffer et al., 2018). However, no clear relation was observed between carbonyl index and the sorption of PCBs (Endo et al., 2005), aromatic hydrocarbons (Müller et al., 2018; Hüffer et al., 2018) and ethers (Müller et al., 2018) to MPs. Aging seems to have little influence when absorption is involved, as changes in the surface are not likely to affect absorption (Müller et al., 2018). Hüffer et al. (2018) found a decrease in sorption to UV-aged PS for polar and non-polar organic chemicals, because the oxidation of the aged surface of PS powder favored the reaction with water by hydrogen bonds and the formation of clusters of water molecules, together with a non-significant increase in surface area. Still, non-polar chemicals had higher distribution coefficients than had polar ones, indicating the importance of hydrophobic interactions.

Beside the aging of MPs, the co-existence of chemical contaminants in the environment may also affect sorption if the competition for sorption sites occurs. Even though many studies tested a mixture of chemicals (Turner & Holmes, 2015; Velzeboer et al., 2014; Fries & Zarfl, 2012; Beckingham & Ghosh, 2017), to our knowledge only the work by Bakir et al. (2012) has evaluated sorption in single and combined exposures of two chemicals (DDT and phenanthrene). The sorption of DDT to both PVC and PE powders (200–250 μm) was higher and independent of phenanthrene presence, while the competition to binding sites limited phenanthrene sorption to PVC but not to PE (Bakir et al., 2012). Therefore, the competition between sorbates in the field can also result in lower sorption capacity in comparison to lab studies, which it is likely to be dependent on sorbate and MP properties.

6. Partitioning of chemicals in soil in the presence of MPs

A large number of studies have investigated the presence and effects of microplastics in the aquatic compartment, especially in the marine environment. However, sediment and soil are also important sinks for MPs. In sediments, few studies have been conducted to assess the quantities and interactions of MPs by using passive samplers (Velzeboer et al., 2014), by performing MP filtration from sediment and subsequent analysis (Teuten et al., 2007), or by mass balance modeling (Kleinteich et al., 2018). To our knowledge, no studies on the sorption of chemicals to MPs have been performed yet in soil.

Nevertheless, increasing awareness of soils as a final destination for microplastics is observed. The amount of plastic waste retained in the continent is estimated to be 4 to 23 times higher than the amount released to the oceans (Horton et al., 2017). One important route of MPs (and many other contaminants) to soils is the application of biosolids. It has been estimated that up to 430,000 tons of microplastics can end up in agricultural lands in Europe, through the application of biosolids (Nizzetto et al., 2016). Thus, the assessment of MP interactions with other chemicals in biosolids and soils and its consequences for chemical bioavailability in soil are urgently needed.

With the increasing input of microplastics in soils, it is important to consider the possibility of microplastics to bind chemicals compared to other compartments of the soil. Previously, a mass balance model has been used to assess the importance of MPs in the distribution of hydrophobic organic chemicals between compartments in the marine environment (Koelmans et al., 2016) and in freshwater sediments (Kleinteich et al., 2018). Here, we use a mass balance model for estimating the partitioning of PCBs and phenanthrene (Phe) in soil in the presence of microplastics. Using porewater, soil, dissolved organic carbon, biota and plastic as the environmental compartments, the distribution of the total amount (in mg) of a chemical in soil (Q_t) can be described as:

$$Q_t = C_w V_w + C_w M_s K_d + C_w M_{doc} K_{doc} + C_w M_b K_{bio} + C_w M_{pl} K_{pl}$$

where C_w is the concentration in porewater (mg/L) and V_w the volume of porewater (L), M_s, M_{doc}, M_b and M_{pl} are the masses, in kg, of soil, dissolved organic carbon, biota (in terms of lipid) and microplastics, respectively. K_d, K_{doc}, K_{bio} and K_{pl} are the partitioning coefficients compartment-porewater for soil, DOC, biota, and microplastics in L/kg. K_{bio} in fact is the bioconcentration factor (BCF) expressed on a lipid basis, so given as L/kg lipid.

The mass of a chemical in compartment i can be calculated by dividing the amount in that compartment i (M_iK_i) by the total amount, cancelling out C_w. To get the total amount of the chemical in microplastics, the equation can be rewritten to read:

$$Q_{tpl} = M_{pl}K_{pl} / (V_w + M_sK_d + M_{doc}K_{doc} + M_bK_{bio} + M_{pl}K_{pl})$$

The following assumptions were made: (1) the air compartment was not included; (2) the microplastic compartment was considered to consist of only one material (e.g., polyethylene, polyvinyl chloride or polypropylene); (3) partitioning processes were considered to be linear in all cases and at equilibrium; (4) K_d values for sediment were chosen due to the lack of data for soil and in order to use K_d and K_{pl} values from the same study.

The parameters used in the model can be found in Tables SI–2. The mass of microplastics (M_{pl}) was defined as the microplastic amount entering agricultural lands from biosolids. According to Ng et al. (2018), in Europe a lifetime input between 2.3 and 15.8 ton/ha of microplastics end up in the top 100 mm layer of agricultural soils from biosolids. We used these values of M_{pl} for best and worst case scenarios, respectively.

A single biosolid application in Europe can give a dose of 0.63 ton MP/ha/y. Considering an area of 1 ha (or 10,000 m^2) and 100 mm topsoil, this dose ends up in a soil volume of 1000 m^3. With an average soil density of 1400 kg/m^3, this corresponds with a mass of soil (M_s) of 1.4×10^6 kg. The volume of porewater (V_w) was calculated as 25% of soil dry weight, corresponding to 350,000 L. In this volume of porewater, with an average dissolved organic carbon level of 33 mg/L (De Troyer et al., 2014), the total mass of DOC (M_{doc}) is 11.55 kg. For the biota compartment, the mass was expressed as the lipid concentration in soil, assuming that living organisms make up 10% of the soil organic matter and that their lipid content is 1% of their body mass (Jager, 1998).

For PCBs, the partitioning coefficients to sediment and microplastic were taken from Velzeboer et al. (2014). To verify the distribution of different congeners, the PCBs with the highest and lowest microplastic-water coefficients (K_{pl}) from this study were used: PCB 169 and PCB 44 with a log K_{pl} of 7.31 and 4.68, respectively. The K_{doc} was estimated from the equation $\log K_{doc} = 0.72 \log K_{ow} + 0.87$ (from Karickhoff et al. (1979) in Evans (1988)), and PCB uptake in earthworms was estimated using the equation presented in Jager (1998): BCF = 0.93 K_{ow} - 3.01.

For phenanthrene, the K_{pl} for polyethylene (PE), polyvinyl chloride (PVC) and polypropylene (PP) were taken from Teuten et al. (2007), with values of 38100, 1650 and 2190 L/kg, respectively. The K_d of 135 L/kg for phenanthrene (Phe) in sediment was taken from the same study. The log K_{doc} for Phe was 4.70 L/kg (Mott, 2002), log BCF in earthworms was 3.9 L/kg (Jager et al., 2000).

Fig. 1 shows the distribution of PCBs and Phe in the different compartments. The major amount of the chemicals was found to be bound to the soil compartment. For PCBs, microplastics are the second compartment with the highest proportions in both best and worst case scenarios, with 2% of the PCBs being sorbed to microplastics in the latter one. For Phe, the distribution varied greatly among the different scenarios, and was mainly dependent on MP composition. In the worst case scenario, up to 23% of Phe was

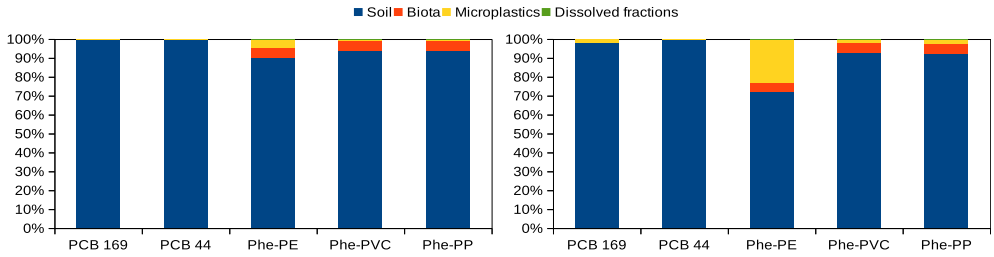

Fig. 1. Best (left) and worst (right) case scenarios for the distribution of PCBs and phenanthrene (Phe) in the compartments soil, dissolved fractions (pore water and dissolved organic carbon), biota and microplastics. For PCBs, the partitioning coefficient for polyethylene was used, while for phenanthrene partitioning coefficients for polyethylene (Phe-PE), polyvinyl chloride (Phe-PVC) and polypropylene (Phe-PP) were used.

bound to PE microplastics, which was caused by the high K_{pl} for PE (38100 L/kg) in comparison to a low K_d for soil (135 L/kg). Also in this scenario, the proportion of Phe bound to PVC and PP was small at 1.3 and 1.7%, respectively. In the best case scenario, the amount of Phe bound to the microplastic compartment decreased to 4% for PE and to ~0.2% for PVC and PP.

The amount of chemical found in the other compartments, biota, water and DOM, showed little difference between the different scenarios or types of microplastic. For both PCBs, negligible amounts were detected in these compartments in all cases, while for Phe up to 0.2% were observed in water and DOM. The proportion of Phe in the biota compartment was more significant, ranging from 4.2 to 5.5%.

We are aware that different results may be obtained in real soils. For example, assuming that all plastics will constitute of PE leads to an overestimation of the partitioning of Phe to the MP compartment, since PE presented much higher K_d values in comparison to PP and PVC (Teuten et al., 2007). Moreover, a linear sorption may overestimate the partitioning to solid phases, as it considers that absorption is the dominant process. However, if the sorption process is non-linear, it can be restricted to the availability of the sorption sites on the microplastic surface.

When modeling the mass balance of PCB 169 in the ocean, Koelmans et al. (2016) found that only 0.0002% is likely to partitioning to microplastics, while the majority (98%) is likely to be in the water compartment. As pointed out by these authors, the product of M_iK_i determines the importance of the compartment i. The mass of water in the ocean was 13 orders of magnitude higher than microplastic mass (Koelmans et al., 2016). Thus, the proportion bound to microplastics was much lower, even though a higher partitioning coefficient K_{pl} was used.

The mass of microplastics used in the present study was only 3 to 4 orders of magnitude lower than the mass of soil. This may explain the higher fraction of chemical binding to MPs in soil in comparison to the aquatic compartment (Gouin et al., 2011; Koelmans et al., 2016). Here, the MPs accounted for 0.1% of the total amount of soil in the worst case scenario, which is in the range (0.03–6%) of microplastics found in an industrial area in Australia (Fuller & Gautam, 2016). Our results are in agreement with Kleinteich et al. (2018), who also used a mass balance model to assess the distribution of phenanthrene and anthracene in freshwater sediment in the presence of MPs. They found that more than 80% of the chemicals were in sediment, with around 15% bound to MPs and only 1% partitioned to the water phase.

Although K_{pl} probably was overestimated (as commented above), it is suggested that larger quantities of chemicals may be bound to microplastics in the terrestrial compartment in comparison to marine environments (Koelmans et al., 2016; Gouin et al., 2011). Therefore, microplastics should be looked at as a significant sink of chemicals in the soil compartment, and its potential consequences (i.e., bioaccumulation and biomagnification) for the exposure of soil organisms should be considered.

7. Implications for toxicity and bioaccumulation

7.1. MP effects on chemical contaminant toxicity

The sorption of chemicals to MPs may become a threat to biota when ingestion occurs. Animals collected from aquatic environments found to ingest MPs include copepods (Desforges et al., 2015), polychaetes (Gusmão et al., 2016), and even mussel (van Cauwenberghe and Janssen, 2014) and fish species (Rochman et al., 2015) used for human consumption. In soils, it has been shown that earthworms (Huerta Lwanga et al., 2016; Rodriguez-Seijo et al., 2017) and mealworms (Wu et al., 2018) can ingested MPs. Therefore, it is important to determine the role of MPs in the toxicity of chemical contaminants. In Tables SI-3, SI-4 and SI-5, an overview is given of toxicity studies conducted in marine water, freshwater and sediment/soil, respectively.

A good approach is to test both the single and combined effects and compare the outcomes. For instance, the EC50 for the immobilization of *Daphnia magna* of bisphenol in the presence of PA (5.5 mg/L) did not significantly differ from bisphenol alone (6.5 mg/L) (Rehse et al., 2018). Therefore, PA was a negligible source of bisphenol. Also, no significant difference was found between the EC50s for *D. magna* immobility of phenanthrene alone (0.47 mg/L) and in the presence of irregular PE MPs (0.14 mg/L) (Frydkjær et al., 2017). An increase in the EC50 for cefalexin effects on *Pomatoschistus microps* predatory performance was observed upon combined exposure with PE spheres (5.2 mg/L) compared with single exposure (3.8 mg/L), but the overlap of 95% confidence intervals indicated a lack of significance (Fonte et al., 2016). Similarly, the EC10, EC20 and EC50 of copper for growth inhibition in the algae *Tetraselmis chuii* did not differ from the corresponding ECx when exposed with PE microspheres (Davarpanah & Guilhermino, 2015). And the presence of PS did not affect the toxicity of the pesticides dimethoate and deltamethrin, regarding mortality and immobilization of *D. magna* (Horton et al., 2018). Altogether, these results indicate that PA, PS and PE MPs did not affect the toxicity of the mentioned chemicals to aquatic organisms.

For other chemicals, MP presence may decrease contaminant toxicity. Due to the strong sorption of glyphosate to PS-NH_2 nanospheres, an antagonistic effect on growth of the algae *Microcystis aeruginosa* was observed by Zhang et al. (2018b). Phenanthrene and 17α-ethinylestradiol sorption to PVC decreased their bioavailability to zebrafish as well, as indicated by gene expression (Sleight et al., 2017). On the other hand, an increase in the toxicity of chemical contaminants when exposed with MPs can occur, depending on the endpoint analyzed or treatment method (Brandts et al., 2018; Ranieri et al., 2018; Zhang et al. 2019a; Kim et al., 2017; Ma et al., 2016; Kleinteich et al., 2018). For this reason, a summary of the effects of MP on the analyzed endpoints (i.e., increasing,

decreasing or no change in the chemical contaminant toxicity) is presented in Tables SI-3, SI-4 and SI-5.

As surface properties of MPs may affect sorption, Kim et al. (2017) evaluated the effects of PS and PS-COOH on nickel toxicity to *D. magna*. PS and Ni showed slight antagonistic effects, and PS-COOH and Ni showed synergistic effects. The higher effect of the functionalized surface was not related to sorption, as similar sorption levels were observed for both MPs. It could be related to the higher toxicity of PS-COOH itself, as in the single MP experiments the EC50 for PS-COOH (25 mg/L) was significantly lower than that for PS (42 mg/L) (Kim et al., 2017). Due to COOH functionalization, nano-PS was suspended in water as hydrogen bonds are formed with water molecules (Velzeboer et al., 2014), which could have enhanced the toxicity of PS-COOH to *D. magna* in comparison to PS.

In the sorption studies discussed in the previous sections, MP size may have a great effect on sorption capacity. By comparing micro and nanoplastics of different sizes, Ma et al. (2016) found that a smaller particle (50 nm) and phenanthrene combination had additive effects on *D. magna* and also increased the bioaccumulation of phenanthrene by-products. For bigger particles (10 μm), no difference with single phenanthrene toxicity was observed. The authors attributed this finding to the lower adsorption of phenanthrene to 10 μm MP, as the sorption experiment found a higher Freundlich K_f for the 50 nm MP. This is a solid piece of work, as it performed batch sorption experiments to support the toxicity findings.

7.2. MP effects on chemical contaminant bioaccumulation

Chemical characteristics can also affect the sorption to MPs and consequently their uptake and toxicity. PCB congeners were found to have different bioaccumulation patterns in *Arenicola marina* depending on MP concentration, which was related to congener hydrophobicity (Besseling et al., 2013). Also, the uptake of higher brominated PBDEs by the marine amphipod *Allorchestes compressa* was favored in the presence of MPs (Chua et al., 2014). The authors indicated the lower solubility and higher K_{ow} of these compounds as crucial factors for determining their sorption to MPs. This result is in agreement with the findings from sorption experiments, which pointed at factors such as K_{ow}-related hydrophobic forces. However, MPs have been found to not affect Paul-Pont et al. (2016); Devriese et al. (2017); Khan et al. (2015) or even decrease (Khan et al., 2015; Sleight et al., 2017; Chua et al., 2014; Magara et al., 2018) the bioavailability of chemicals.

In Fig. 2, possible scenarios for the effects of MPs on the uptake/bioaccumulation of chemicals are presented. In the first scenario (Fig. 2B), the presence of MPs does not affect bioaccumulation, being similar to the single exposure to the chemical (Fig. 2A). This can be related to: (1) a low affinity between chemical and MPs leading to a low sorption capacity; (2) a low MP uptake by the organism; or (3) the fraction accumulated from MPs is negligible compared with uptake from other routes of exposure. In an experiment with zebrafish (*Danio rerio*), the lack of an effect of MPs on Ag bioaccumulation was explained from the insufficient time for Ag sorption to MPs and to the tendency of MPs to float on the surface (Khan et al., 2015). So, we can conclude that both low sorption levels and low MP uptake could be the reason for such result. Fluoranthene bioaccumulation in mussels (*Mytilus* spp.) was also not affected by MPs, since proportionally smaller amounts of fluoranthene from MPs were taken up in comparison with uptake from water and food (Paul-Pont et al., 2016). The distribution and bioavailability of the chemical, therefore, would be the same with or without the MPs.

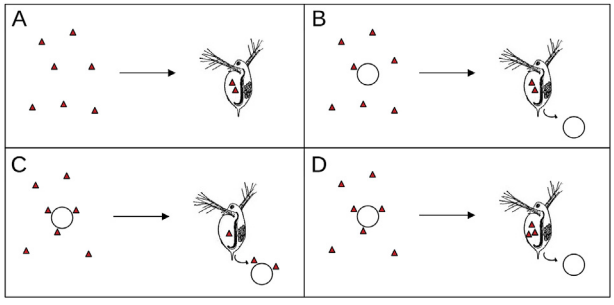

Fig. 2. Three possible scenarios of a chemical contaminant bioaccumulation (number of ▲) due to microplastic (○; MP) ingestion in comparison to a single exposure (Fig. 2A). The microplastics may not affect the bioaccumulation (Fig. 2B). However, it can also be a sink of the chemical, decreasing bioaccumulation (Fig. 2C) or act as a vector and increase the bioaccumulation (Fig. 2D).

In the following scenario (Fig. 2C), MPs act as a sink for the chemical contaminant and decrease its bioaccumulation. Sorption of the chemical to MPs is relevant, but somehow the sorbed fraction is less available. This can be due to a strong sorption to MPs as was observed for the bioaccumulation of PDBEs in amphipods (Chua et al., 2014) and bifenthrin in *Chironomus tepperi* (Ziajahromi et al., 2019) exposed to PE MPs. Similarly, the pre-incubation of the chemical with MPs prior the exposure may decrease bioavailability due to a strong sorption and low desorption during the exposure. This has been found for fluoranthene (Magara et al., 2018) and Ag (Khan et al., 2015) pre-sorbed to PE MPs, decreasing the bioaccumulation in mussels and zebrafish, respectively. Also, a low desorption from the MPs in the organism's gut can lead to this result (Paul-Pont et al., 2016). Therefore, the gut conditions are also of major importance regarding desorption of chemicals from MPs, and potential chemical accumulation by the organisms. A decrease in bioaccumulation, giving final results such as presented in Fig. 2C, could also be obtained with the ingestion of “clean” MPs. As shown in Mohamed Nor & Koelmans (2019), PCBs were transferred from contaminated food to clean PE MPs in a simulated gut condition.

In soils, a decrease in hydrophobic organic contaminant (HOC) bioaccumulation in the presence of PE and PS MPs (≥1% w/w) was observed in the earthworm *Eisenia fetida* (Wang et al., 2019). This result was attributed to the decrease in free HOC concentration in porewater due to the sorption of HOC to the MPs. However, no effect of MPs on HOC bioaccumulation was found in two situations. The first was found in earthworms exposed to low MP concentration (0.1% w/w), which showed no difference from controls (i.e., worms exposed only to HOC in soil). Also, no effects of MPs (from 0.1 to 10% w/w) was observed in the bioaccumulation of phenanthrene. Phenanthrene was the least hydrophobic compound, with lowest K_{oc} and K_{pl}, and also can be rapidly transformed by the earthworms (Wang et al., 2019). These results are in agreement with the findings from the previous section (Partitioning of chemicals in soil in the presence of MPs), showing the importance of MP concentration and partitioning coefficients of the contaminants.

The final scenario (Fig. 2D) shows the MPs acting as a vector for bioaccumulation. In this case, high sorption levels combined with MP uptake and chemical desorption in the gut result in increased bioaccumulation. A fast desorption rate of organic compounds is expected under gut conditions (Bakir et al., 2014a; Coffin et al., 2019; Mohamed Nor & Koelmans et al., 2015). Therefore, this scenario is very likely if higher sorption of the contaminant to MPs together with high MP ingestion rate occur. By increasing MP concentration from 1 mg/L to 50 mg/L, a higher amount of venlafaxine was found in the liver of the pond fish *Misgurnus anguillicaudatus*, which may be a consequence of incidental MP uptake by

the fish with increasing MP concentration (Qu et al., 2018).

It should be emphasized, however, that most studies reviewed here did not observe an increased bioaccumulation of chemicals in the presence of MPs. This is in agreement with the findings of Koelmans et al. (2016) who concluded that the role of MPs as a route of uptake for organic contaminants by marine organisms is negligible in comparison to other routes, such as the dietary route. Moreover, more complex and realistic media can weaken the effects of MPs on bioaccumulation, as shown by Ziajahromi et al. (2019): In synthetic water, MP presence decreased the toxicity of bifenthrin in *Chironomus tepperi*, while the organic fraction in river water mitigated any influence of MPs.

The influence of MPs on chemical uptake and elimination rates seems to be important indeed as delayed effects might be observed. The combined exposure of pyrene and PE MPs resulted in a delayed mortality of the fish *P. microps* (Oliveira et al., 2013). The median lethal time (LT50) for pyrene changed from ~30 h in the single exposure to ~40 h in the presence of PE spheres (Oliveira et al., 2013). At the end of an experiment, the organisms might still contain MPs inside the gut, and it is possible that further effects may be observed during depuration. Higher histopathological damage and higher fluoranthene concentration in the digestive glands was found in the mussel *Mytilus* spp. when exposed to fluoranthene in the presence of PS MPs in comparison to fluoranthene single exposure after 7 days of depuration (Paul-Pont et al., 2016). Prior to the depuration (i.e., at the end of the experiment), fluoranthene single was found to be more toxic than its mixture with PS (Paul-Pont et al., 2016). More studies are needed to better understand the possible effects of MPs on the toxicodynamics of chemical contaminants.

As pointed out by Phuong et al. (2016), MPs with irregular shapes (fragments and fibres) are the most abundant microplastics in the environment, yet microspheres and beads are the most used in toxicity tests on marine organisms. Similarly, most MPs used are microspheres (see Tables SI-3 to SI-5). It is understandable that these particles can be purchased and their spherical shapes facilitate the detection in the samples or inside the organisms, however, it has been shown that shape can affect the results of sorption studies. Therefore, the use of irregular shapes should be encouraged in order to obtain a more realistic view on the topic.

Regarding toxicity studies, a full dose-response study should be conducted to address the effects of MPs on organisms when possible (van Gestel & Selonen, 2018). And in the case of testing a co-exposure of MPs and chemical contaminants, the experiment should be design to allow some kind of comparison between single and combined toxicities. For example, Zhang et al. (2019a) evaluated the acute effects and oxidative stress of PS (1 and 10 μm) and roxithromycin to *D. magna*, however, calculated the LC50 only for the single exposures. Had the authors calculated the LC50 for roxithromycin in combination with MPs, for example, a better understanding on possible synergy or antagonism could be observed.

Finally, many procedures should be considered which are not covered in standard protocols for toxicity testing. Incubating or not the MPs with the chemical prior to exposure and adding a depuration period seemed to be the most important issues. Pre-sorbing the chemicals on MPs may result in a lower bioavailability, but it can provide a more realistic exposure scenario (Khan et al., 2015). Depuration time after the exposure can give insights into the (delayed) effects caused by MPs, especially because MPs can affect the bioaccumulation kinetics of chemicals.

8. Conclusion

Even though the number of studies is increasing, the sorption of chemical contaminants to MPs is a very complex subject and much remains to be understood. The influence of MP and chemical properties on sorption has been investigated in more detail, while the influence of medium characteristics and effects of MP aging need to be further addressed.

Sorption studies are important as they can identify the chemicals with higher affinity to MPs under different environmental conditions. Overall, hydrophobic compounds are attracted by hydrophobic forces to the neutral areas on the MP surface, while hydrophilic or charged compounds are attracted to the negative areas on the MP surface with electrostatic interactions and media characteristics being most important. It should also be kept in mind that laboratory studies are likely to result in shorter times to reach equilibrium in comparison to field studies, and that aging and biofilm formation on the MP surface can lead to increased sorption.

Sorption studies were also essential for the mass balance model. The sorption capacities could be used for estimating the distribution of chemicals in an environment containing a significant quantity of MPs. In contrast to marine environments, where low quantities of chemicals are partitioned to MPs, much higher amounts were found in soils. Therefore, more studies on MPs in the soil compartment should be conducted, aiming to assess chemical partitioning and toxicity.

The toxicity outcomes agree to some extent with the sorption data. However, a higher sorption to MPs does not always lead to higher toxicity or bioaccumulation of a contaminant. Even though MPs may not act as a vector for bioaccumulation, there is some indication that they are likely to affect the kinetics of uptake and depuration of chemical contaminants in organisms, as well as the mechanisms of toxicity at the molecular and physiological level.

Conflicts of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.06.030.

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